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PAPER

Multiple bonding *versus* cage formation in organophosphorus compounds: the gas-phase structures of tricyclo-$P_3(CBu^t)_2Cl$ and $P{\equiv}C{-}Bu^t$ determined by electron diffraction and computational methods†

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The gas-phase structures of tricyclo-$P_3(CBu^t)_2Cl$ and $P{\equiv}C{-}Bu^t$ have been determined by electron diffraction and associated quantum chemical calculations. Efforts to obtain detailed solid-state data for tricyclo-$P_3(CBu^t)_2Cl$ have been thwarted by inability to prepare suitable crystalline material. Additional calculations for another tricyclic isomer of $P_3(CBu^t)_2Cl$ and for two phosphorus-containing cyclopentadiene derivatives with pseudo-planar five-membered rings show that the experimentally observed isomer is more stable by at least 52 kJ mol^{-1}. Calculations for the equivalent structures with P atoms replaced by CH fragments have demonstrated that a ring structure is more favourable by over 200 kJ mol^{-1} compared to each of two cage structures.

Introduction

The concept of phosphorus behaving as a carbon copy has proved a useful tool for rationalising much of the chemistry of low-coordinate phosphorus.[1] Within the family of five-membered rings, there are clear similarities between the cyclopentadienyl anion, $[C_5H_5]^-$, and its phosphorus-substituted analogues, $[P_n(CH)_{5-n}]^-$, although detailed examination draws out some subtle but important differences between the all-carbon species and the heterocyclic anions. On consideration of the phosphorus-containing analogues of the neutral C_5H_6, notable differences emerge. The most stable form of C_5H_6 is cyclopentadiene, whereas an isolobal triphosphorus analogue, $P_3(CBu^t)_2Cl$ (**1**), first reported by the groups of Binger and Regitz in 1991,[2] was formulated as having a tricyclic structure consisting of a P–C singly-bonded framework. This assertion was made on the basis of three ^{31}P NMR resonances at δ 234.7, −121.4 and −302.2 ppm, which relate to the three magnetically distinct environments of P(1), P(4) and P(5), respectively, in the tricyclic framework (Fig. 1a). Compound **1** is itself prepared by the reaction of $Zr(\eta^5\text{-}C_5H_5)_2[P_2(CBu^t)_2]$ with PCl_3.[3]

We have used this molecule as a starting point for several diverse studies and have shown that it provides an atom-efficient route to the triphospholide anion, $[P_3(CBu^t)_2]^-$,[4,5] as well as a route to a species that is a triphosphorus analogue of the cyclopentadienyl cation.[5] Furthermore, the distinctive ^{31}P NMR signature of **1** in combination with DFT calculations has been utilised to show that nucleophilic substitution of **1** occurs *via* competing S_N2-type

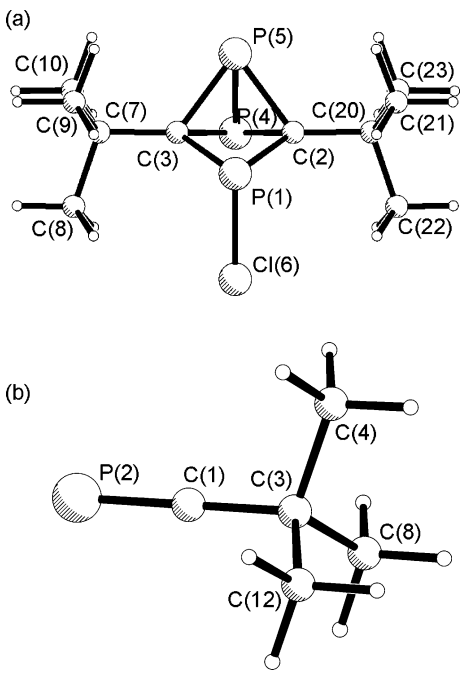

Fig. 1 Molecular structures, including numbering scheme, for (a) tricyclo-$P_3(CBu^t)_2Cl$, **1**, and (b) $P{\equiv}C{-}Bu^t$. Hydrogen-atom numbering has been omitted for clarity.

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and AE′ reaction pathways, the latter being a previously unseen substitution pathway in phosphorus chemistry.[6,7] In order to rationalise these observations fully it was clear that knowledge of the precise topology of **1** was required. Whereas we were able to use X-ray diffraction to characterise tricyclic $P_3(CBu^t)_2I$,[6] our efforts to obtain detailed structural data on $P_3(CBu^t)_2Cl$ have been thwarted by an inability to prepare suitable crystalline material. Here we describe the gas-phase structure of **1** determined by electron diffraction and some associated quantum chemical calculations. P≡C–Bu^t, **2**, is an important precursor to many phosphorus-containing analogues of well-known organic molecules. It was first synthesised by Becker and co-workers more than 30 years ago,[8–10] when its gas-phase structure was determined by joint analysis of electron-diffraction and microwave-spectroscopic data.[11] Here we have repeated the electron diffraction experiment and analysed this in conjunction with the original rotation constant, yielding a P≡C bond length that is significantly different from that found in the original study.

Experimental

Gas-phase electron diffraction (GED)

Data were collected for **1** and **2** using the Edinburgh gas-phase electron diffraction (GED) apparatus.[12] An accelerating voltage of 40 kV was used, resulting in an electron wavelength of approximately 6.0 pm.

For **1** and **2**, scattering intensities were recorded on Kodak Electron Image films at two nozzle-to-film distances to maximise the scattering angle over which data were collected. For **1**, in order to obtain suitable vapour pressures, and to prevent condensation in the nozzle, the sample and nozzle were heated to 373 and 394 K, respectively, for the longer nozzle-to-film distance and 403 and 418 K for the shorter distance. For **2** data were collected with the nozzle held at room temperature and the sample cooled to 236 K in order to control the vaporisation.

The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for both camera distances for both **1** and **2** are given in Table S1.† Also included are the electron wavelengths determined using the scattering patterns for benzene, which were recorded immediately after the sample patterns. The photographic films were scanned using an Epson Expression 1680 Pro flatbed scanner as part of a method that is now used routinely in Edinburgh and described elsewhere.[13] The data-reduction and least-squares refinement processes were carried out using the ed@ed v2.4 program[14] employing the scattering factors of Ross *et al.*[15]

Computational methods

All calculations were performed using the resources of the NSCCS[16] and the EaStCHEM Research Computing Facility[17] running the Gaussian 03 suite of programs.[18] A single minimum on the potential-energy surface of tricyclo-$P_3(CBu^t)_2Cl$ was identified as representing a C_s-symmetric structure. As no real structures were found with the chlorine atom endo to the P(1)C(2)P(4)C(3) ring (see Fig. 1a) such structures were not considered further. With this symmetry fixed, geometries were optimised first at the Hartree–Fock level of theory with the 3-21G* basis set[19] on all atoms followed by the 6-31G* basis set[20] and then using MP2[21] to include the energy due to electron correlation. At this level the 6-311G* and 6-311+G* basis sets[22] were also used. Force constants calculated at the MP2/6-311+G* level were subsequently used along with the program SHRINK[23] to obtain initial amplitudes of vibration and distance correction terms for use in the GED refinement.

Calculations were also performed for an isomeric form of tricyclo-$P_3(CBu^t)_2Cl$ and two monocyclic forms of $P_3(CBu^t)_2Cl$ at the same levels of theory to provide information about the relative stabilities of the tricyclic and monocyclic forms.

For P≡C–Bu^t the minimum-energy structure was found to have C_{3v} symmetry. Geometry optimisations and force-constant calculations were performed at the same levels of theory as for **1**. Because of a seeming lack of agreement between the published gas-phase structure of **2**, the structure determined in this work, and various calculated structures calculations were also performed using CCSD and CCSD(T) levels of theory.[24,25]

Results

GED Studies

On the basis of the calculations described above, a C_s-symmetric model was written describing tricyclo-$P_3(CBu^t)_2Cl$. A number of assumptions were made about the *tert*-butyl groups in order to minimise the number of parameters that were fitted to the GED data. All C–C distances to the methyl groups were assumed to be identical (they differed only by a few tenths of a picometre in the calculations), and the groups were assigned local C_s symmetry, with C(3)–C(7)–C(9) being equal to C(3)–C(7)–C(10). The geometry was described in terms of 18 refineable parameters, comprising seven bond lengths and differences, eight angles and differences and three torsion-angle parameters (Table 1). The atom numbering used in the descriptions of the parameters is shown in Fig. 1a. When writing the model it was useful to imagine the structure as consisting of a non-planar four-membered ring consisting of P(1), C(2), C(3) and P(4), with P(5) lying on the C_s mirror plane above the ring. To help in defining parameters an additional point, X, was defined as lying at the mid-point of the vector C(2)···C(3), and this was used as the origin of the coordinate system. The axes were chosen so that C(2) and C(3) lie on the *x* axis and P(5) on the *y* axis.

As two different types of C–C bond lengths (C_{tert}–C_{Me} and C_{tert}–C_{ring}) exist in **1** and as all three symmetrically unique C_{tert}–C_{Me} are calculated to be very similar in length the average value of all C–C distances (weighted to account for the three C_{tert}–C_{Me} bonds) and the difference between the mean C_{tert}–C_{Me} and C_{tert}–C_{ring} distances were used as parameters (p_{1-2}). A single distance (p_3) was employed for all C–H bonds throughout. The three different P–C distances were described using the average of P(1)–C(2), P(4)–C(2) and P(5)–C(2) (p_4), and two difference parameters {[P(1)–C(2) + P(4)–C(2)]/2 – P(5)–C(2)} and [P(1)–C(2) – P(4)–C(2)] (p_{5-6}). The final distance parameter required was P–Cl (p_7). The heavy-atom structure of the *tert*-butyl groups was calculated to have the angles C(3)–C(7)–C(9) and C(3)–C(7)–C(10) identical and that for C(3)–C(7)–C(8) significantly different. The average value for these two different angles and the difference between them were used in the model (p_{8-9}). All C–C–H angles in the methyl groups were

Table 1 Refined (r_{h1}) and calculated[a] (r_e) geometric parameters for tricyclo-$P_3(CBu^t)_2Cl$, **1**, from the GED study[b]

	Parameter	r_{h1}	r_e	Restraint
Independent				
p_1	$(rC_{tert}–C_{ring} + 3\times rC_{tert}–C_{Me})/4$	154.07(6)	152.8	—
p_2	$(rC_{tert}–C_{ring}) – (C_{tert}–C_{Me})$	0.96(37)	1.9	1.9(5)
p_3	*r*C–H	110.5(2)	109.5	—
p_4	*r*P–C average	186.93(7)	187.6	—
p_5	*r*P–C difference 1	–5.6(5)	–5.6	–5.6(5)
p_6	*r*P–C difference 2	–3.8(5)	–3.9	–3.9(5)
p_7	*r*P(1)–Cl	216.6(15)	214.8	—
p_8	[∠C(3)–C(7)–C(8) + ∠C(3)–C(7)–C(10)]/2	109.2(2)	109.5	—
p_9	∠C(3)–C(7)–C(10) – ∠C(3)–C(7)–C(8)	1.3(5)	1.2	1.2(5)
p_{10}	∠C–C–H	108.1(6)	109.5	109.5(1)
p_{11}	∠X–P(1)–Cl	106.6(9)	107.3	—
p_{12}	∠C(2)–P(5)–C(3)	72.9(2)	71.5	—
p_{13}	∠X–C(3)–C(7)	0.1(9)	1.5	—
p_{14}	∠C(8)–C(7)–C(10)	108.8(9)	109.3	109.3(10)
p_{15}	∠C(8)–C(7)–C(9)	109.6(9)	109.7	109.7(10)
p_{16}	ϕP(5)–X–C(2)–P(4)[c]	90.5(7)	92.0	—
p_{17}	ϕP(1)–X–C(2)–P(5)[c]	–124.3(5)	–123.7	—
p_{18}	ϕP(5)–C(3)–C(7)–C(8)	–174.6(23)	–161.3	—
Dependent				
p_{19}	*r*C(3)–C(7)	153.35(28)	151.4	—
p_{20}	*r*C(7)–C(8)	154.31(11)	153.5	—
p_{21}	*r*P(1)–C(2)	183.2(3)	183.8	—
p_{22}	*r*P(4)–C(2)	187.0(3)	187.7	—
p_{23}	*r*C(3)–P(5)	190.6(3)	191.3	—
p_{24}	*r*P(4)–P(5)	214.6(13)	220.2	—
p_{25}	∠C(3)–C(7)–C(8)	108.5(3)	109.0	—
p_{26}	∠C(3)–C(7)–C(10)	109.8(4)	110.1	—

[a] Refers to an MP2/6-311+G* calculation. [b] Distances (*r*) are in pm, angles (∠) in degrees. See text for parameter definitions and Fig. 1a for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits. [c] X lies at the midpoint of the C(2)···C(3) vector.

calculated to be very similar, so a single value (p_{10}) was used. The position of the chlorine atom, which lies in the C_s mirror plane, was described using the angle X–P(1)–Cl (p_{11}). The angle C(2)–P(5)–C(3) (p_{12}) was included to define the position of P(5) above the ring and ∠X–C(3)–C(7) (p_{13}) defined the deviation of the *tert*-butyl groups from a starting point where C(3)–C(7) lies in the C(2)C(3)P(4) plane, with a positive angle indicating a shift perpendicular to the plane in the direction of P(5). Two internal C–C–C angles ($p_{14–15}$) from the *tert*-butyl group were used along with p_8 and p_9 to calculate the position of the *tert*-butyl group. Dihedral angle ϕP(5)–X–C(2)–P(4) (p_{16}) was chosen to place the phosphorus atom above the ring, ϕP(1)–X–C(2)–P(5) was used in a similar manner to drop P(1) out of the C(2)C(3)P(4) plane and ϕP(5)–C(3)–C(7)–C(8) defined the twist of the *tert*-butyl group about the C(3)–C(7) bond.

All independent geometric parameters were refined using a least-squares method and restraints were applied, using the SARACEN method,[26] to parameters that could otherwise not be refined (Table 1). The restraints were based on values calculated at the MP2/6-311+G* level and the uncertainties were derived from the changes in value of each parameter during the series of calculations that were performed. In addition, 11 groups of amplitudes of vibration were refined. See Table S2† for lists of amplitudes of vibration. The success of the refinement can be assessed numerically using the final *R* factor, which was R_G = 0.082 (R_D = 0.071), and visually using the radial-distribution and difference curves (Fig. 2a), and the molecular-scattering intensity curves (Fig. S1†). The least-squares correlation matrix is given in Table S3† and coordinates for the final GED structure and for the calculated structure (MP2/6-311+G*) are in Tables S4 and S5, respectively.†

As was the case for **1**, P≡C–Bu^t has two different types of C–C distance that must be modelled, as shown in Table 2 ($p_{2–3}$). As well as these C–C distances the other two distances that are used are *r*C≡P (p_1) and *r*C–H (p_4). As the molecule has C_3 point-group symmetry only a single CCC angles is required to describe the geometry (p_5). Two different CCH angles are modelled as a weighted average and difference ($p_{6–7}$) to account for the hydrogen atoms that lie in the C_3 mirror plane (one per methyl group) and for those that lie out of the plane (two per methyl group). Finally, the HCH angle is used to complete the definition of the symmetric methyl groups (p_8).

Again the SARACEN method[26] was used to restrain parameters that could otherwise not be refined. As well as the eight geometrical parameters that were refined, nine amplitudes of vibration were refined (see Table S6†). Finally, the vibrationally corrected rotation constant, B_z, which was published as part of the previous study of **2**, was included as an extra datum.[11] This has a value of 1653.70 MHz, and the restraint of 0.005 MHz was determined using the experimental uncertainty and the magnitude of the correction applied. The final *R* factor for the refinement of P≡C–Bu^t was R_G = 0.047 (R_D = 0.028) and the inclusion, or otherwise, of the rotation constant had very little effect on this value. Its inclusion did, however, reduce the ESD on the P≡C bond length. Table 2 contains the refined parameters and details of the SARACEN restraints that were applied. The radial-distribution curve is shown in Fig. 2b, and the molecular-scattering intensity curves in Fig. S2.† The least-squares correlation matrix is given

Table 2 Refined (r_{h1}) and calculated[a] (r_e) geometric parameters for P≡C–Bu^t from the present GED study as well as from the original study in 1981 (r_{av})[b]

	Parameter	r_{h1}	r_e	Restraints	r_{av}
		this work			ref. 11
Independent					
p_1	rC≡P	155.00(11)	157.1	—	153.6(2)
p_2	r\{[C_{tert}–C(1)] + 3×[C_{tert}–C_{Me}]\}/4	152.55(7)	152.1	—	—
p_3	r\{[C_{tert}–C_{Me}] – [C_{tert}–C(1)]\}	6.6(2)	6.6	6.6(4)	—
p_4	rC–H	109.0(2)	109.5	—	108.0(3)
p_5	∠CCC	108.9(1)	109.1	—	109.0(2)
p_6	∠\{[CCH_{ip}] + 2×[CCH_{oop}]\}/3	110.9(2)	110.5	110.5(6)	—
p_7	∠(CCH_{oop} – CCH_{ip})	1.0(3)	1.0	0.5(3)	—
p_8	∠HCH	108.5(5)	108.5	108.5(5)	108.8(5)
Dependent					
p_9	$r$$C_{tert}$–$C_{Me}$	154.21(8)	153.7	—	154.3(2)[c]
p_{10}	$r$$C_{tert}$–C(1)	147.59(17)	147.1	—	147.3(4)[c]
p_{11}	∠CCH_{ip}	110.2(3)	109.8	—	—
p_{12}	∠CCH_{oop}	111.3(2)	110.8	—	—

[a] Refers to an MP2/6-311+G* calculation; see Discussion for more details about calculations. [b] Distances (r) are in pm, angles (∠) in degrees. See text for parameter definitions and Fig. 1b for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits. [c] These parameters were independently refined in the original study.

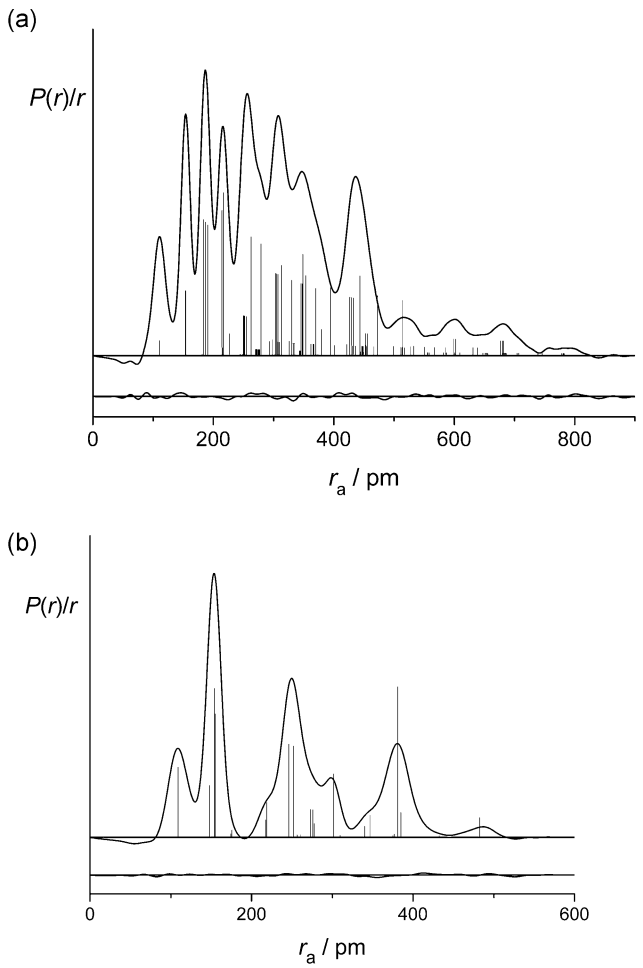

Fig. 2 Experimental radial-distribution curve and theoretical-minus-experimental difference curve for the refinement of (a) tricyclo-$P_3(CBu^t)_2Cl$, **1**, and (b) P≡C–Bu^t, **2**. Before Fourier inversion the data were multiplied by s·exp(–0.00002s^2)/($Z_P - f_P$)($Z_C - f_C$).

in Table S7† and coordinates for the final GED structure and for the calculated structure (MP2/6-311+G*) are in Tables S8 and S9,† respectively.

Discussion

$P_3(CBu^t)_2Cl$ (**1**) has been shown experimentally to exist as a tricyclic cage in the gas phase (Fig. 1a). As well as this minimum-energy isomer there is one other possible tricyclic cage, in which the CBu^t groups are adjacent, and in principle there can also be two isomers with the three phosphorus atoms and two carbon atoms in a cyclopentadiene-like ring. These are shown in Fig. 3. No energy minima were found for structures with the two CBu^t groups adjacent in a five-membered ring. All three of the additional isomers are significantly higher in energy than the minimum-energy form. At the MP2/6-311+G* level the tricyclic form (**3**) is higher in energy by 52 kJ mol^{-1}, the structure where the PCl moiety sits between the two CBu^t groups (**4**) is 65 kJ mol^{-1} higher in energy, while that where the PCl is adjacent to only one CBu^t group (**5**) is 61 kJ mol^{-1} less stable. Cartesian coordinates and energies for each of these isomers are given in Tables S10–S12.†

We have run calculations (MP2/6-311+G*) for the structures of analogues of each of **2**, **3**, **4**, and **5** in which the P atoms are replaced by CH fragments. Although an analogue of **4** can be imagined, no minimum-energy structure could be found (probably because the smaller ring dimensions force the Cl and *tert*-butyl groups to become too close); this showed that the preferred structure for cyclobutadiene with two *tert*-butyl groups is the analogue of structure **5**. This ring was more than 200 kJ mol^{-1} lower in energy than either of the cage structures calculated. In this system, therefore, phosphorus cannot really be considered as a carbon copy.

The gas-phase structure of P≡C–Bu^t (**2**) has been redetermined using new electron-diffraction data supplemented by the existing rotational constant.[11] The 1981 joint GED and microwave spectroscopic study found the P≡C bond length (r_{av}; error limit 2σ) to be 153.6(2) pm. It was, therefore, slightly surprising

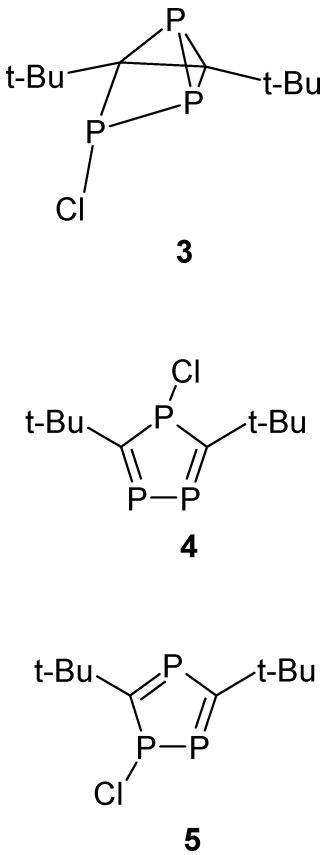

Fig. 3 Schematics for further isomers of $P_3(CBu^t)_2Cl$.

that our new study yielded the significantly larger value of 155.00(11) pm. For comparison, the X-ray diffraction structure of **2** yielded a bond length of 154.8(1) pm.[27] At the time that our refinement was completed the highest level calculation available to us was MP2/6-311+G*, which gave a value of 157.1 pm, further complicating matters. Unfortunately, attempts to perform calculations using either CCSD or CCSD(T) with a substantial basis set were not feasible. It was, however, possible to compare P≡C as calculated using CCSD/6-31G* (155.5 pm) with that using MP2/6-31G* (157.3 pm). This demonstrated that the MP2 method is overestimating the bond length, perhaps accounting for the discrepancy between the experimental distance in this work and the MP2/6-311+G* value described above.

As calculations for P≡C–Bu^t were proving to be too computationally demanding, we instead performed a series of calculations for P≡C–CH_3. For this molecule we were able to perform calculations using CCSD(T) (albeit with the small 6-31G* basis set), which showed that the P≡C distance was around 0.6 pm shorter when using this method rather than MP2. We believe that our newly refined P≡C bond length is a sensible value, and that the very big discrepancies between calculated distances show that this quantity is nowhere near converged.

Acknowledgements

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